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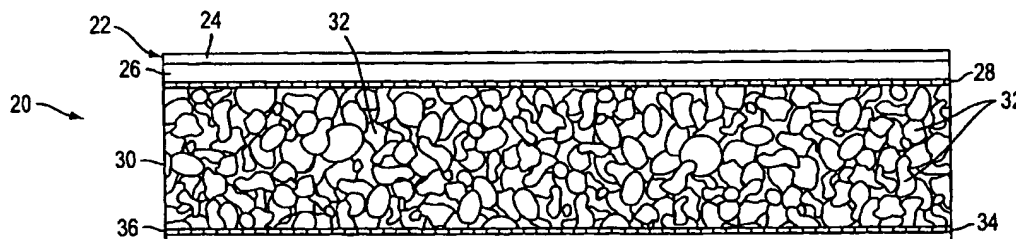
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(54) Title: CO-EXTRUDED THERMOPLASTIC LAMINATE



(57) Abstract: A thermoplastic multi-layer composite structure (20) is disclosed and consists in a first embodiment of a co-extruded acrylic polypropylene outer skin (22) and high melt strength polypropylene substrate (26) which is attached to a first surface of a polypropylene foam core (30). The foam core can either be constructed from an expanded polypropylene or an extruded polypropylene. Where an expanded polypropylene foam core is provided, the foam core is attached to the outer and inner skin through the use of a polypropylene adhesive (28 and 34).

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CO-EXTRUDED THERMOPLASTIC LAMINATEBACKGROUND OF THE INVENTION1. Field of the Invention

The present invention relates generally to co-extended thermoplastic laminates
5 containing a polyolefin graft copolymer and one or more layers of polyolefin material.

2. Description of the Prior Art

Thermoplastic composite materials are well known and used in various
industries including the marine industry

10 In the marine industry, as well as numerous other industries, the use of
fiberglass as a construction material is highly prevalent. Fiberglass is defined as a
material consisting of extremely fine filaments of glass that can be embedded in
various resins to make boat hulls, fishing rods, and the like. The fine filaments of
glass can also be combined in yarn and woven into fabrics or used in masses as a
15 thermal and acoustical insulator. Fiberglass wool, a thick, fluffy material made from
discontinuous fibers, is used for thermal insulation and sound absorption. The
fiberglass wool is often found in ship and submarine bulkheads and hulls, as well as
automobile engine compartments and body panel liners.

The major ingredients of fiberglass include silica sand, limestone, and soda
20 ash. The silica sand is used as the glass former, and the limestone and soda ash are
provided primarily to lower the melting temperatures. Other ingredients can also be
utilized and are usually provided to improve certain properties such as chemical
resistance.

Other structural parts, especially large structural parts, are typically made from
25 an acrylonitrile/butadiene/styrene rubber (ABS). When weatherability is required, a
laminate of ABS and a layer of acrylonitrile/styrene/acrylic resin (ASA) or an acrylic
resin is used.

Laminates have also been produced from various combinations of polyolefin
materials. However, they lack the required rigidity, scratch and mar resistance, and
30 gloss after thermoforming.

SUMMARY OF THE INVENTION

The present invention provides for a co-extruded laminate including a top skin and at least one layer of a polyolefin substrate, preferably a high melt strength polypropylene.

- 5 In one embodiment, the present invention provides a co-extruded polyolefin laminate having a hard, high modulus top layer including at least one layer of a graft copolymer made from a polyolefin, such as a polypropylene polymer material, onto which is graft polymerized acrylic and/or styrenic monomers and at least one other layer formed from a propylene homopolymer, a random propylene copolymer, a
10 random propylene terpolymer, an olefin polymer composition, a thermoplastic olefin, or a combination of two or more of such polymers or polymer compositions, optionally blended with a high melt strength polypropylene.

- Composite materials are also contemplated and these include at least one layer of the co-extruded laminate and, for instance, a low density polyolefin foam layer
15 (such as, for example, less than about 0.300 kg/m³). The composite materials can be used to fabricate large structural parts such as by thermoforming.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

- In a preferred embodiment the co-extruded laminate comprises a graft modified polyolefin outer layer as a top skin and at least one polyolefin as a substrate.
20 The graft modified polyolefin is preferably an acrylic polypropylene. An amorphous material can also be added to the acrylic polypropylene outer layer to increase the impact strength of top skin. Preferably, the substrate is a polyolefin having a high melt strength, preferably a polypropylene. The top skin thus preferably includes an acrylic polypropylene as an outer layer and high melt strength polypropylene layer as
25 a substrate. The top skin can also be referred to as a cap sheet. The outer layer provides a relatively hard and weatherable outer surface. The substrate is provided as backing to the outer layer for cost purposes. Where cost considerations are of less concern a top skin can alternatively be constructed solely of acrylic polypropylene.

- Furthermore, the top skin can be prepared from a relatively high density
30 polypropylene, with or without substrate, and without the acrylic component in the outer layer. The density of outer layer is preferably higher than the density of substrate. The high density polypropylene provides a hard and stiff surface, which for

some uses of composite structure may be sufficient without the need of an additional acrylic element or substrate. Preferably, the top skin, including the outer layer with or without substrate, is obtained by extrusion (outer layer solely) or co-extrusion (outer layer and substrate) procedures with top skin being in the form of a planar sheet.

- 5 When co-extruded, the outer layer and substrate travel through a die where they are heated and fused together to form top skin. Preferably, the outer layer is relatively thin as compared to substrate.

Once constructed, top skin can be vacuumformed or thermoformed to its intended shape, assuming that the planar sheet form is not the intended shape. In one vacuumforming method, an extruded or co-extruded top skin is loaded on a clamp
10 frame and rotated in a first oven station for heating (preheat) the planar sheet. The preheated sheet is placed in a second oven station, which causes the sheet to sag and become molten plastic, preferably softened but not melted *per se*. A mold of the intended shape is disposed below the sagging sheet. The sheet is lowered into the
15 mold and a vacuum is applied through the base of the mold to suck the sheet about the mold. The pulled sheet takes the form of the mold. The shaped sheet is then allowed to cool and removed from the mold, to provide a top skin in its intended shape.

As to the co-extrusion embodiment, suitable materials can, in principle, be selected from a current edition of Plastics, Thermoplastics and Thermosets (extruding and molding grades).
20

Our co-extruded laminate can be comprised of:

- (1) at least one layer (e.g. an outer layer) of a graft copolymer comprising a backbone of a propylene polymer material, having graft polymerized thereto polymerized monomers selected from the group consisting of
25 (a) at least one acrylic monomer,
(b) at least one styrenic monomer, and
(c) mixtures of (a) and (b), and
(2) at least one layer (substrate) of a polyolefin material selected from the group consisting of:
30 (a) a crystalline homopolymer of propylene having an isotactic index greater than 80;
(b) a crystalline random copolymer of propylene and an olefin selected from the group consisting of ethylene and C₄-C₁₀ α -olefins, provided that when the

olefin is ethylene, the maximum polymerized ethylene content is 10% by weight, and when the olefin is a C₄-C₁₀ α-olefin, the maximum polymerized content thereof is 20% by weight, the copolymer having an isotactic index greater than 85;

5 (c) a crystalline random terpolymer of propylene and two olefins selected from the group consisting of ethylene and C₄-C₈ α-olefins, wherein the maximum polymerized C₄-C₈ α-olefin content is 20% by weight, and, when ethylene is one of the olefins, the maximum polymerized ethylene content is 5% by weight, the terpolymer having an isotactic index greater than 85;

10 (d) an olefin polymer composition comprising:

(i) about 10 parts to about 60 parts by weight of a crystalline propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) propylene and ethylene, (b) propylene, ethylene and a C₄-C₈ α-olefin, and (c)
15 propylene and a C₄-C₈ α-olefin, the copolymer having a propylene content of more than 85% by weight and an isotactic index greater than 85;

(ii) about 5 parts to about 25 parts by weight of a copolymer of ethylene and propylene or a C₄-C₈ α-olefin that is insoluble in xylene at ambient temperature; and

20 (iii) about 30 parts to about 70 parts by weight of an elastomeric copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α-olefin, and (c) ethylene and a C₄-C₈ α-olefin, wherein the copolymer optionally contains about 0.5% to about 10% by weight of a diene, contains less than 70% by weight of ethylene, and is soluble in xylene at ambient temperature and has an intrinsic viscosity of about 1.5 to about 4.0 dl/g;

25 in which the total of (ii) and (iii), based on the total olefin polymer composition is from about 50% to about 90%, and the weight ratio of (ii)/(iii) is less than 0.4, and wherein the composition is prepared by polymerization in at least two stages and has a flexural modulus of less than 150 MPa;

30

(e) a thermoplastic olefin comprising:

(i) about 10% to about 60% of a propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene and a C₄-C₈ α-olefin, and (c) ethylene and a C₄-C₈ α-olefin, wherein the copolymer has a propylene content greater than 85% and an isotactic index of greater than 85%;

(ii) about 20% to about 60% of an amorphous copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α-olefin, and (c) ethylene and a C₄-C₈ α-olefin, the copolymer optionally containing about 0.5% to about 10% of a diene and containing less than 70% ethylene and being soluble in xylene at ambient temperature; and

(iii) about 3% to about 40% of a copolymer of ethylene and propylene or a C₄-C₈ α-olefin that is insoluble in xylene at ambient temperature, wherein the composition has a flexural modulus of greater than 150 but less than 1200 MPa;

(f) a heterophasic polyolefin composition comprising:

(i) about 30% to about 98% of a polymeric material selected from the group consisting of a polypropylene homopolymer having an isotactic index greater than 90, and a crystalline copolymer having an isotactic index greater than 85 of propylene and at least one α-olefin of the formula CH₂=CHR, where R is H or a C₂-C₆ alkyl group, and the α-olefin is less than 10% of the copolymer when R is H and is less than 20% when R is a C₂-C₆ alkyl group or a combination thereof with R = H, and

(ii) about 2% to about 70% of an elastomeric copolymer of propylene and an α-olefin of the formula CH₂=CHR, where R is H or a C₂-C₈ alkyl group, the α-olefin is about 45% to about 75% of the elastomeric copolymer, and about 10% to about 40% of the elastomeric copolymer is insoluble in xylene at ambient temperature, or an elastomeric copolymer of ethylene and a C₄-C₈ α-olefin having an α-olefin content of about 15% to about 60%;

(g) mixtures of two or more of (2)(a) to (2)(f); and

(h) mixtures of one or more of (2)(a) to (2)(g) and about 5% to about 40% of a high melt strength propylene polymer material having strain hardening elongational viscosity, and

5 wherein about 5% to about 85% of the total thickness of the laminate comprises the graft copolymer layer (1).

Our co-extruded laminates of this invention have a lower density, better weather resistance, better chemical resistance, greater toughness, and better scratch and mar resistance than materials currently available for making large thermoformed
10 structural parts. They can also be recycled, have good thermal processing stability, are easy to pigment, and can be buffed or sanded to remove scratches. Any number of materials can be selected for the various layers, making it possible to design a wide variety of materials with whatever combination of properties is desired in the finished product. This combination of properties is not possible when using a single layer
15 sheet.

Propylene polymers, commonly referred to as polypropylenes, are generally described in the Encyclopedia of Polymer Science and Engineering, Volume 13, pages 464-531 (John Wiley & Sons, 1988) and, for example, in Polymeric Materials Encyclopedia, Vol. 9, pages 6578-6623 and 631-6656 (CRC Press 1996). In general,
20 propylene polymer materials that can be used as the backbone of the graft copolymer in layer (1) of the laminate of our invention include, by way of example:

(a) a crystalline homopolymer of propylene having an isotactic index greater than 80, preferably about 85 to about 99;

(b) a crystalline random copolymer of propylene and an olefin selected from
25 the group consisting of ethylene and C₄-C₁₀ α -olefins, wherein when the olefin is ethylene, the maximum polymerized ethylene content is 10% by weight, preferably about 4%, and when the olefin is a C₄-C₁₀ α -olefin, the maximum polymerized content thereof is 20% by weight, preferably about 16%, and wherein the copolymer has an isotactic index greater than 85;

30 (c) a crystalline random terpolymer of propylene and two olefins selected from the group consisting of ethylene and C₄-C₈ α -olefins, wherein the maximum polymerized C₄-C₈ α -olefin content is 20% by weight, preferably about 16%, and, when ethylene is one of the olefins, the maximum polymerized ethylene content is 5%

by weight, preferably about 4%, the terpolymer having an isotactic index greater than 85;

d) an olefin polymer composition comprising:

- 5 (i) about 10 parts to about 60 parts by weight, preferably about 15 parts to about 55 parts, of a crystalline propylene homopolymer having an isotactic index greater than 80, preferably about 85 to about 98, or a crystalline copolymer selected from the group consisting of (a) propylene and ethylene, (b) propylene, ethylene and a C₄-C₈ α-olefin, and (c) propylene and a C₄-C₈ α-olefin, the copolymer having a propylene content of more than 85% by weight, 10 preferably about 90% to about 99%, and an isotactic index greater than 85;
- (ii) about 5 parts to about 25 parts by weight, preferably about 5 parts to about 20 parts, of a copolymer of ethylene and propylene or a C₄-C₈ α-olefin that is insoluble in xylene at ambient temperature; and
- 15 (iii) about 30 parts to about 70 parts by weight, preferably about 20 parts to about 65 parts, of an elastomeric copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α-olefin, and (c) ethylene and a C₄-C₈ α-olefin, the copolymer optimally containing about 0.5% to about 10% by weight of a diene, and containing less than 70% by weight, preferably about 10% to about 60%, most preferably about 12% to 20 about 55%, of ethylene and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 4.0 dL/g;

the total of (ii) and (iii), based on the total olefin polymer composition being from about 50% to about 90%, and the weight ratio of (ii)/(iii) being less than 0.4, preferably 0.1 to 0.3, wherein the composition is prepared by polymerization in at

25 least two stages and has a flexural modulus of less than 150 MPa; and

(e) a thermoplastic olefin comprising:

- 30 (i) about 10% to about 60%, preferably about 20% to about 50%, of a propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene and a C₄-C₈ α-olefin, and (c) ethylene and a C₄-C₈ α-olefin, the copolymer having a propylene content greater than 85% and an isotactic index of greater than 85%;

- (ii) about 5 parts to about 25 parts by weight, preferably about 5 parts to about 20 parts, of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature; and
- (iii) about 30 parts to about 70 parts by weight, preferably about 20 parts to about 65 parts, of an elastomeric copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% by weight of a diene, and containing less than 70% by weight, preferably about 10% to about 60%, most preferably about 12% to about 55%, of ethylene and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 4.0 dl/g;
- the total of (ii) and (iii), based on the total olefin polymer composition being from about 50% to about 90%, and the weight ratio of (ii)/(iii) being less than 0.4, preferably 0.1 to 0.3, wherein the composition is prepared by polymerization in at least two stages and has a flexural modulus of less than 150 MPa; and
- (i) about 10% to about 60%, preferably 20% to about 50%, of a propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer having a propylene content greater than 85% and an isotactic index of greater than 85%;
- (ii) about 20% to about 60%, preferably about 30% to about 50%, of an amorphous copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% of a diene, and containing less than 70% ethylene and being soluble in xylene at ambient temperature; and
- (iii) about 3% to about 40%, preferably about 10% to about 20%, of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature,
- wherein the composition has a flexural modulus of greater than 150 but less than 1200 MPa, preferably about 200 to about 1100 MPa, and most preferably about 200 to about 1000 MPa.

As referred to herein, room or ambient temperature is -25°C

The $\text{C}_4\text{-C}_8$ α -olefins useful in the preparation of (1)(d) and (1)(e) include, for example, butene-1; pentene-1; hexene-1; 4-methyl-1-pentene, and octene-1.

The diene, when present, is typically one that would be suitable use in for making an EPDM, such dienes include a butadiene; 1,4-hexadiene; 1,5-hexadiene, or ethylenenorbornene.

Propylene polymer materials (1)(d) and (1)(e) can be prepared by polymerization in at least two stages, where in the first stage the propylene, or propylene and ethylene or an α -olefin, or propylene, ethylene and an α -olefin are polymerized to form component (i) of (1)(d) or (1)(e), and in the following stages the mixtures of ethylene and propylene or the α -olefin, or ethylene, propylene and the α -olefin, and optionally a diene, are polymerized to form components (ii) and (iii) of (1)(d) or (1)(e).

The polymerization can be conducted in liquid phase, gas phase, or liquid-gas phase using separate reactors, all of which can be done either by batch or continuously. For example, it is possible to carry out the polymerization of component (i) using liquid propylene as a diluent, and the polymerization of components (ii) and (iii) in gas phase, without intermediate stages except for the partial degassing of the propylene. All gas phase is the preferred method.

The preparation of propylene polymer material (1)(d) is described in more detail in U.S. Patent Nos. 5,212,246 and 5,409,992, which preparation is incorporated herein by reference. The preparation of propylene polymer material (1)(e) is described in more detail in U.S. Patent Nos. 5,302,454 and 5,409,992, which preparation is incorporated herein by reference.

Acrylic monomers that can be graft polymerized onto the propylene polymer material backbone include, for example, acrylic acid; acrylate esters, such as the methyl, ethyl, hydroxyethyl, 2-ethylhexyl, and butyl acrylate esters; methacrylic acid, and methacrylate esters such as the methyl, ethyl, butyl, benzyl, phenylethyl, phenoxyethyl, epoxypropyl, hydroxypropyl methacrylate esters, and mixtures thereof.

Styrenic monomers that can be graft polymerized onto the propylene polymer material backbone include, for example, styrene and alkyl or alkoxy ring-substituted styrenes where the alkyl or alkoxy group is a C_{1-4} linear or branched alkyl or alkoxy group, and mixtures thereof.

When a mixture of acrylic and styrenic monomers is used, the ratio of acrylic to styrenic monomers can be about 95/5 to about 5/95.

During the graft polymerization, the monomers also polymerize to form a certain amount of free or ungrafted polymer or copolymer. Any reference to
5 "polymerized monomers" in this specification is meant to include both grafted and ungrafted polymerized monomers. The polymerized monomers comprise from about 10 parts to about 120 parts per hundred parts of the propylene polymer material, preferably about 30 to about 95 pph. The morphology of the graft copolymer is such that the propylene polymer material is the continuous or matrix phase, and the
10 polymerized monomers, both grafted and ungrafted, are a dispersed phase.

The graft copolymer can be made according to any one of various methods. One of these methods involves forming active grating sites on the propylene polymer material either in the presence of the grafting monomers, or followed by treatment with the monomers. The grafting sites can be produced by treatment with a peroxide
15 or other chemical compound that is a free radical polymerization initiator. Preparation of graft copolymers by contacting the polypropylene with a free radical polymerization initiator such as an organic peroxide and one or more vinyl monomers is described in more detail in U.S. Patent No. 5,140,074, which preparation is incorporated herein by reference. Grafting sites can also be produced by irradiating
20 an olefin polymer with high energy ionizing radiation. Preparation of graft copolymers by irradiating an olefin polymer and then treating with a vinyl monomer is described in U.S. Patent No. 5,411,994, which preparation is incorporated herein by reference. The olefin polymers that can be grafted include homopolymers of C_2-C_8 α -olefins, as well as random copolymers of C_2-C_8 α -olefins and C_2-C_{10} α -olefins.
25 The free radicals produced on the polymer as a result of the chemical or irradiation treatment form the active grafting sites on the polymer and initiate the polymerization of the monomers at these sites. Graft copolymers produced by peroxide-initiated grafting methods are preferred.

The graft copolymer layer (1) can also optionally comprise a rubber
30 component selected from one or more of the group consisting of (i) an olefin copolymer rubber, (ii) a monoalkenyl aromatic hydrocarbon-conjugated diene block copolymer rubber, and (iii) a core-shell rubber. Any of these rubber components can

have acid or anhydride functionality or can be free of these functional groups. The preferred rubber components are (i) and (ii), either alone or in combination.

When present, the rubber component is used in an amount of about 2% to about 40%, preferably about 2% to about 15%, by weight.

5 Suitable polyolefin rubbers include, for example, saturated polyolefin rubbers such as ethylene/propylene monomer rubbers (EPM, ethylene/octene-1, and ethylene/butene-1 rubbers, and unsaturated polyolefin rubbers such as ethylene/propylene/diene monomer rubbers (EPDM). The preferred olefin copolymer rubbers are ethylene/propylene, ethylene/ butene-1, and ethylene/octene-1
10 copolymers. The most preferred rubbers for use with an acrylic-grafted polypropylene material are ethylene/butene-1 and ethylene/octene-1 copolymer rubbers. The most preferred rubbers for use with a styrenic-grafted propylene polymer material are ethylene/propylene, ethylene/butene-1, ethylene/octene-1, or a combination of either of these rubbers with a block copolymer rubber.

15 The monoalkenyl aromatic hydrocarbon conjugated diene block copolymer can be a thermoplastic elastomer of the A-B (or diblock) structure, the linear A-B-A (or triblock) structure, the radial (A-B)_n type where n = 3-20%, or a combination of these structure types, wherein each A block is a monoalkenyl aromatic hydrocarbon polymer block, and each B block is an unsaturated rubber block. Various grades of
20 copolymers of this type are commercially available. The grades differ in structure, molecular weight of the mid and end blocks, and ratio of monoalkenyl aromatic hydrocarbon to rubber. The block copolymer can also be hydrogenated. Typical monoalkenyl aromatic hydrocarbon monomers are styrene, ring-substituted C₁-C₄ linear or branched alkyl styrenes, and vinyltoluene. Styrene is preferred. Suitable
25 conjugated dienes include, for example, butadiene and isoprene. Preferred block copolymers are hydrogenated styrene/ethylene-butene-1/styrene triblock copolymers.

 The weight average molecular weight, M_w , of the block copolymers generally will be in the range of about 45,000 to about 260,000 g/mole, M_w of about 50,000 to about 125,000 g/mole being preferred on the basis that they afford blend compositions
30 having the best balance of impact strength and stiffness. Also, while block copolymers having unsaturated as well as saturated rubber blocks can be used, copolymers having saturated rubber blocks are preferred, also on the basis of the impact/stiffness balance of the compositions containing them. The weight ratio of monoalkenyl aromatic

hydrocarbon to conjugated diene rubber in the block copolymer is in the range of about 5/95 to about 50/50, preferably about 10/90 to about 40/60.

The core-shell rubber components comprise small particles of crosslinked rubber phase surrounded by a compatibilizing shell, normally a glassy polymer or
5 copolymer. The core is typically a diene rubber such as butadiene or isoprene, or an acrylate. The shell is typically a polymer of two or more monomers selected from styrene, methyl methacrylate, and acrylonitrile. Particularly preferred core-shell rubbers have an acrylate core.

Another optional ingredient in layer (1) is a propylene polymer material.
10 When present, it is used in an amount of about 5% to about 70%, preferably about 10% to about 50%, most preferably about 10% to about 30%, by weight. If this optional ingredient is present, it is selected from the same propylene polymer materials that can be used as the backbone polymer for the graft copolymer, and it can be the same material as the propylene polymer backbone used to prepare the graft
15 copolymer or a different propylene polymer material.

The preferred propylene polymer material is a propylene homopolymer having a broad molecular weight distribution (BMWD PP). The BMWD PP has a M_w/M_n of about 5 to about 60, preferably about 5 to about 40; a melt flow rate of about 0.5 to about 50, preferably about 1 to about 30 g/10 min. and xylene insolubles at 25°C of
20 greater than or equal to 94%, preferably greater than or equal to 96%, and most preferably greater than or equal to 98%. The propylene polymer material having a broad molecular weight distribution can be a homopolymer of propylene or an ethylene/propylene impact-modified homopolymer of propylene, wherein the propylene homopolymer has a broad molecular weight distribution.

25 The BMWD propylene polymer material can be prepared by sequential polymerization in at least two stages, in the presence of a Ziegler-Natta catalyst supported on magnesium halide in active form. The polymerization process occurs in separate and consecutive stages, and in each stage polymerization takes place in the presence of the polymer and the catalyst coming from the preceding stage.

30 The polymerization process can be carried out in a batch or in a continuous mode according to known techniques, operating in liquid phase in the presence or not of an inert diluent, or in gas phase, or liquid-gas phase, preferably in gas phase. The preparation of the BMWD propylene polymer material is described in more detail in U.S. Patent No. 5,286,791, which preparation is incorporated herein by reference.

Either the optional rubber component or the optional ungrafted propylene polymer material can be used by itself, or both of the optional components can be added.

5 About 5% to about 85% of the total thickness of the laminate comprises the graft copolymer layer.

The polyolefin materials that can be used in the at least one layer (2) of the laminate of our invention include:

(a) a crystalline homopolymer of propylene having an isotactic index greater than 80, preferably about 85 to about 99;

10 (b) a crystalline random copolymer of propylene and an olefin selected from the group consisting of ethylene and C₄-C₁₀ α -olefins, wherein when the olefin is ethylene, the maximum polymerized ethylene content is 10% by weight, preferably about 4%, and when the olefin is a C₄-C₁₀ α -olefin, the maximum polymerized content thereof is 20% by weight, preferably about 16%, the copolymer having an isotactic index greater than 85;

15 (c) a crystalline random terpolymer of propylene and two olefins selected from the group consisting of ethylene and C₄-C₈ α -olefins, wherein the maximum polymerized C₄-C₈ α -olefin content is 20% by weight, preferably about 16%, and, when ethylene is one of the olefins, the maximum polymerized ethylene content is 5% by weight, preferably about 4%, the terpolymer having an isotactic index greater than 85;

(d) an olefin polymer composition comprising:

20 (i) about 10 parts to about 60 parts by weight, preferably about 15 parts to about 55 parts, of a crystalline propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) propylene and ethylene, (b) propylene, ethylene and a C₄-C₈ α -olefin, and (c) propylene and a C₄-C₈ α -olefin, the copolymer having a propylene content of more than 85% by weight and an isotactic index greater than 85;

30 (ii) about 5 parts to about 25 parts by weight, preferably about 5 parts to about 20 parts, of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature; and

(iii) about 30 parts to about 70 parts by weight, preferably about 20 parts to about 65 parts, of an elastomeric copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene, and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% by weight of a diene, and containing less than 70% by weight of ethylene and being soluble in xylene at ambient temperature and having an intrinsic viscosity of about 1.5 to about 4.0 dl/g;

the total of (ii) and (iii), based on the total olefin polymer composition, being from about 50% to about 90%, and the weight ratio of (ii)/(iii) being less than 0.4, wherein the composition is prepared by polymerization in at least two stages and has a flexural modulus of less than 150 MPa;

(e) a thermoplastic olefin comprising:

(i) about 10% to about 60%, preferably about 20% to about 50%, of a propylene homopolymer having an isotactic index greater than 80, or a crystalline copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer having a propylene content greater than 85% and an isotactic index of greater than 85%;

(ii) about 20% to about 60%, preferably about 30% to about 50%, of an amorphous copolymer selected from the group consisting of (a) ethylene and propylene, (b) ethylene, propylene and a C₄-C₈ α -olefin, and (c) ethylene and a C₄-C₈ α -olefin, the copolymer optionally containing about 0.5% to about 10% of a diene, and containing less than 70% ethylene and being soluble in xylene at ambient temperature, and

(iii) about 3% to about 40%, preferably about 10% to about 20%, of a copolymer of ethylene and propylene or a C₄-C₈ α -olefin that is insoluble in xylene at ambient temperature,

wherein the composition has a flexural modulus of greater than 150 but less than 1200 MPa, preferably about 200 to about 1100 MPa, and most preferably about 200 to about 1000 MPa;

(f) a heterophasic polyolefin composition comprising:

- 5 (i) about 30% to about 98%, preferably about 60% to about 80%, of a polymeric material selected from the group consisting of a polypropylene homopolymer having an isotactic index greater than 90, and a crystalline copolymer having an isotactic index greater than 85 of propylene and at least one α -olefin of the formula $\text{CH}_2=\text{CHR}$, where R is H or a $\text{C}_2\text{-C}_6$ alkyl group, the α -olefin is less than 10% of the copolymer when R is H and is less than 20% when R is a $\text{C}_2\text{-C}_6$ alkyl group or a combination thereof with R = H; and
- 10 (ii) about 2% to about 70%, preferably about 20% to about 40%, of an elastomeric copolymer of propylene and an α -olefin of the formula $\text{CH}_2=\text{CHR}$, where R is H or a $\text{C}_2\text{-C}_8$ alkyl group wherein the elastomeric copolymer has, having an α -olefin content of about 45% to about 75%, preferably about 50% to about 70%, and most preferably about 60% to about 70%, of the elastomeric copolymer, and about 10% to about 40% of the elastomeric copolymer is insoluble in xylene at ambient temperature, or an elastomeric copolymer of ethylene and a $\text{C}_4\text{-C}_8$ α -olefin having an α -olefin content of about 15% to about 60%, preferably about 15% to about 40%;

20 (g) mixtures of two or more of (2)(a) to (2)(f); and

(h) mixtures of one or more of (2)(a) to (2)(g) with about 5% to about 40% of a high melt strength propylene polymer material having strain hardening elongational viscosity.

Room or ambient temperature means -25°C .

25 The total amount of polymerized ethylene in (2)(d) is preferably about 10% to about 40% by weight.

The C_{4-8} α -olefins useful in the preparation of (2)(d) and (2)(e) include, for example, 1-butene, 1-pentene; 1-hexene; 4-methyl-1-pentene, and 1-octene.

The diene, when present, is, as stated elsewhere herein, typically a butadiene; 30 1,4-hexadiene; 1,5-hexadiene, or ethylenenorbornene.

Propylene polymer materials (2)(d) and (2)(e) can be prepared by polymerization in at least two stages. In the first stage the propylene, or propylene and ethylene or α -olefin, or propylene, ethylene and the α -olefin are polymerized to

term component (i) of (2)(d) or (2)(e). In the following stages the mixtures of ethylene and propylene or the α -olefin, or ethylene, propylene and the α -olefin, and optionally a diene, are polymerized to form components (ii) and (iii) of (2)(d) or (2)(e).

5 The polymerization can be conducted in liquid phase, gas phase, or liquid-gas phase using separate reactors, all of which can be done either by batch or continuously. For example, it is possible to carry out the polymerization of component (i) using liquid propylene as a diluent, and the polymerization of components (ii) and (iii) in gas phase, without intermediate stages except for the
10 partial degassing of the propylene. All gas phase is the preferred method.

 The preparation of propylene polymer material (2)(d) is described in more detail in U.S. Patent Nos. 5,212,246 and 5,409,992, which preparation is incorporated herein by reference. The preparation of propylene polymer material (2)(e) is described in more detail in U.S. Patent Nos. 5,302,454 and 5,409,992, which preparation is
15 incorporated herein by reference.

 The C₂-C₈ olefin in (2)(f) include, linear and branched α -olefins such as, for example, 1-butene; isobutylene; 1-pentene; 1-hexene; 1-octene; 3-methyl-1-butene; 4-methyl-1-pentene; 3,4-dimethyl-1-butene, and 3-methyl-1-hexene.

 The heterophasic polyolefin composition (2)(f) can be obtained by sequential
20 polymerization of monomers in the presence of Ziegler-Natta catalysts, or by mechanical blending of components (i) and (ii). The sequential polymerization process is described in more detail in U.S. Patent No. 5,486,419, which preparation is incorporated herein by reference.

 The high melt strength propylene polymer material used in (2)(h) is preferably
25 a normally solid, high molecular weight, gel-free, predominantly isotactic, semi-crystalline propylene polymer material, the branching index of which is less than 1, that has strain hardening elongational viscosity.

 The branching index quantifies the degree of long chain branching. The branching index of the propylene polymer material in (2)(h) is preferably less than
30 about 0.9, and most preferably about 0.3 to 0.5. It is defined by the equation:

$$y' = \frac{[IV]_{Br}}{[IV]_{Lin}} Mw$$

wherein g' is the branching index, $[\text{IV}]_{\text{Br}}$ is the intrinsic viscosity of the branched propylene polymer material, and $[\text{IV}]_{\text{Lin}}$ is the intrinsic viscosity of a normally solid, predominantly isotactic, semi-crystalline, linear propylene polymer material of substantially the same weight average molecular weight, and, in the case of
5 copolymers and terpolymers, substantially the same relative molecular proportion or proportions of monomer units.

Intrinsic viscosity, also known as the limiting viscosity number, in its most general sense is a measure of the capacity of a polymer molecule to enhance the viscosity of a solution. This depends on both the size and the shape of the dissolved
10 polymer molecule. In comparing a non-linear polymer with a linear polymer of substantially the same weight average molecular weight, the intrinsic viscosity is an indication of the configuration of the non-linear polymer molecule. The above ratio of intrinsic viscosities is a measure of the degree of branching of the non-linear polymer. A method for determining the intrinsic viscosity of propylene polymer
15 materials is described by Elliott et al., J. App. Poly. Sci., 14, 2947-2963 (1970). The intrinsic viscosity is determined with the polymer dissolved in decalin (i.e. decahydronaphthalene) at 135°C.

Weight average molecular weight can be measured by various procedures. However, the procedure preferably used here is that of low angle laser light scattering
20 photometry, which is disclosed by McConnell in Am. Lab., May 1978, in an article entitled Polymer Molecular Weights and Molecular Weight Distribution by Low-Angle Laser Light Scattering".

Elongational viscosity is the resistance of a fluid or semi-fluid substance to elongation. It is a melt property of a thermoplastic material that can be determined by
25 an instrument that measures the stress and strain of a specimen in the melt state when subjected to tensile strain at a constant rate. One such instrument is described and shown in Fig. 1 of Munstedt, J. Rheology, 23, (4), 421-425 (1979). A commercial instrument of similar design is the Rheometrics RER 9000 extensional rheometer. Molten, high molecule weight, linear propylene polymer material exhibits
30 elongational viscosity which, as it is elongated or drawn at a constant rate from a relatively fixed point, tends to increase for a distance dependent on the rate of elongation, and then to decrease rapidly until it thins to nothing- so called ductile or necking failure. On the other hand, the molten propylene polymer material of this

invention, that is of substantially the same weight average molecular weight and at substantially the same test temperature as the corresponding molten, high molecular weight, linear, propylene polymer material, exhibits elongational viscosity which, as it is elongated or drawn from a relatively fixed point at substantially the same rate of elongation tends to increase over a longer distance, and to break or fail by fracture-
5 so-called brittle or elastic failure. These characteristics are indicative of strain hardening. The more long chain branching the propylene polymer material of this invention has, the greater the tendency of the elongational viscosity to increase as the elongated material approaches failure. This latter tendency is most evident when the
10 branching index is less than about 0.8.

The high melt strength polymers can be made by treating a normally solid, amorphous to predominantly crystalline propylene polymer material without strain hardening elongational viscosity with a low decomposition temperature peroxide or with high energy ionizing radiation in the substantial absence of atmosphere oxygen,
15 for example, in an environment in which an active oxygen concentration of less than about 15% by volume is maintained. The peroxide-treated or irradiated propylene polymer material is then heated or treated with a free radical scavenger in the substantial absence of atmospheric oxygen to deactivate substantially all of the free radicals present in the propylene polymer material. The propylene polymer material
20 can be any of the polyolefin materials (a) to (g) listed as suitable for use in layer (2).

The preparation of these high melt strength propylene polymer materials having strain hardening elongational viscosity is described in more detail in U.S. Patents Nos. 5,047,446; 5,047,485 and 5,414,027, which preparations are incorporated herein by reference.

25 Alternatively, the propylene polymer material used in (2)(h) can be characterized by at least (a) either a M_z of at least 1.0×10^6 or a M_z/M_w ratio of at least 3.0, and (b) either an equilibrium compliance J_{∞} of at least $12 \times 10^{-5} \text{ cm}^2/\text{dyne}$ or a recoverable shear strain per unit stress S_r/S_d at least $5 \times 10^{-5} \text{ cm}^2/\text{dyne}$ at 1 sec^{-1} .

The molecular weight distribution in a sample of the propylene polymer
30 material can be determined by high temperature gel permeation chromatography (GPC). The Waters 150 CV GPC chromatograph can be used at 135°C with trichlorobenzene as the carrier solvent and a set of Waters μ -Styragel HT, 10^3 , 10^4 ,

10⁵ and 10⁶ columns. The solution concentration is 0.2% (w/v) and the flow rate is 1 ml/min.

The Rheological characterization of the propylene polymer materials can be conducted with a programmed Rheometrics Mechanical Spectrometer (RMS-800).

- 5 Resin pellets are compression molded into sheets from which samples are stamped out with a 25 mm diameter circular die. Tests are conducted at 210 ± 1°C using 25 mm parallel plate geometry with a 1.4 mm gap. Creep data are obtained under a constant stress of 1000 dyne/cm² for a period of 0-300 sec. The creep compliance J(t) is given by $J(t) = \tau(t)/\sigma = J_{\infty} + t/\eta_0$ wherein τ represents strain, σ represents stress, J_{∞} represents equilibrium compliance, and η_0 represents zero shear viscosity. The
- 10 equilibrium compliance J_{∞} is a measure of the melt elasticity and is determined by first plotting strain against time at constant stress. The strain as a function of time is divided by the stress to give J(t). J_{∞} is the intercept of the J(t) against time plot.

- The recoverable shear strain per unit stress Sr/S also distinguishes the high
- 15 melt strength propylene polymer material. This quantity is a fundamental measure of melt elasticity. Using the programmed Rheometrics Mechanical Spectrometer, the polymer melt is subjected to clockwise rotational shear strain by the driver and the resulting shear stress S and first normal stress N_1 are measured by a transducer. The shear rate range is 0.01 to 10 s⁻¹, the time before measurement is 2.2 min and the time
- 20 of the measurement is 0.3 min. Normal stress measurements are detained at each shear rate. The recoverable shear strain Sr is detained from the first normal stress difference N_1 :

$$Sr = \frac{N_1}{2S}$$

- 25 The normalized quantity Sr/S , i.e., recoverable shear strain per unit stress is a measure of melt elasticity.

Additives such as fillers and reinforcing agents, pigments slip agents, waxes, oils, antiblocking agents, and antioxidants can also be present in the compositions used to form the layers of the laminates of this invention.

- 30 In the laminates of this invention, many combinations of layers (1) and (2) are contemplated, or example, I-II, I-II-III, and I-II-I, in which I is the graft copolymer, II is one of the polyolefin materials (2)(a) - (2)(h), and III is a polyolefin material selected from (2)(a) - (2)(h) that is different than II. In the laminates of this invention,

layer (1) comprises about 5% to about 85% of the total thickness of the laminate, which is about 50 mils to about 500 mils.

A two layer laminate can comprise a methyl methacrylate/methyl acrylate copolymer, a methyl methacrylate/styrene copolymer, or a polymerized styrenic monomer for layer (1), and a mixture of an impact-modified polypropylene and 5-30% of a high melt strength propylene homopolymer having strain hardening elongational viscosity for layer (2). A three layer laminate can be I-II-III, where I is a methyl methacrylate/methyl acrylate copolymer, a methyl methacrylate/styrene copolymer, or a polymerized styrenic monomer; II is the olefin polymer composition (2)(d), and III is an impact-modified polypropylene. The impact-modified polypropylene can be (1) the heterophasic polyolefin composition (2)(f), where fraction (ii) is an ethylene/propylene copolymer, (2) a blend of propylene homopolymer and an ethylene/propylene, ethylene/butene, or ethylene/octene copolymer rubber, or mixtures thereof, (3) a blend of the polyolefin composition (2)(d) and (1) or (2) above, or (4) a blend of the high melt strength propylene polymer material in (2)(h) and (1), (2) or (3) above.

The laminates can be made by co-extruding the various layers, or a molded part can be made by co-injection molding or thermoforming the laminate.

Co-injection molding is well known to those skilled in the art and means that two or more different thermoplastic materials are "laminated" together as described in Rosato et al., Injection Molding Handbook 2nd Ed., Chapman & Hall, 1008-1011 (1995). Two or more injection units are required, with each material having its own injection unit. The materials can be injected into specially designed molds such as, for example, rotary and shuttle molds. The sandwich configuration that results takes advantage of the different properties that each material contributes to the structure. There are three techniques for molding multicomponent parts called the one-, two-, and three-channel techniques. In the one-channel system, the plastic melts for the compact skins and foam core are injected into the mold one after another by shifting a valve. The two-channel system allows the formation of the compact skin and core material simultaneously. The three-channel system allows simultaneous injection, using a direct sprue gating, of the compact skin and core (foamable or solid).

The thermoforming process is well known to those skilled in the art and is described, for example, in the Encyclopedia of Polymer Science and Engineering, Vol. 16, pages 807-832 (John Wiley & Sons, 1989) and D. V. Rosato, Rosato's

Plastics Encyclopedia and Dictionary, 755-757 (Hanser Publishers 1993). The process usually includes heating a thermoplastic sheet, film, or profile to its softening temperature and forcing the hot and flexible material against the contours of a mold by pneumatic means (differentials in air pressure can be created by pulling a vacuum
5 between the plastic and the mold, or the pressure of compressed air can be used to force the material against the mold), mechanical means (plug or matched mold, for example), or combinations of pneumatic and mechanical means. The process involves (1) heating the sheet in a separate oven and then transferring the hot sheet to a forming press, (2) using automatic machinery to combine heating and forming in a
10 single unit, or (3) a continuous operation feeding off a roll of thermoplastic material or directly from the exit of an extruder die (postforming).

The laminates of this invention exhibit a combination of (1) good gloss, (2) hardness, (3) good plate impact, (4) good thermoformability, and (5) no delamination of layers on impact.

15 Another embodiment of our invention is a composite material comprising (a) at least one layer of the laminate or the thermoformed article of this invention and (b) a layer of a low density polyolefin foam having a density of about 1 to about 15 lbs/ft³ and a thickness of about 1/8 inch to about 4 inches, preferably >1 inch up to 3 inches. The low density foam layer can be an extruded foam sheet, or the layer can be molded
20 from foam beads. The low density foam layer can comprise a single thickness of foam, or several thin layers attached to each other, e.g., thermally, such as by the use of a shot knife, or by the use of a suitable adhesive such as, for example, low molecular weight polyolefins made from a functionalized monomers with polar groups such as monounsaturated carboxylic acids or their anhydride derivatives such
25 as maleic or itaconic acid or their anhydrides, or unfunctionalized monomers; hot melt adhesives, or aqueous- or solvent-based emulsions. Suitable bonding agents include, for example, hydrogenated hydrocarbon resins such as Regalrez series tackifiers, commercially available from Hercules Incorporated, and Arkon P series tackifiers, commercially available from Arakawa Chemical (U.S.A.) Incorporated; 1023PL
30 amorphous polypropylene tackifying agent available from Eastman Chemical Company, and predominantly amorphous ethylene/propylene copolymers commonly known as ethylene/propylene rubber" (EPR). Optionally, (c) a sheet of a polyolefin material such as, for example, a polyethylene or polypropylene sheet, can be applied to the other side of the low density foam layer of the composite material.

The laminate or thermoformed article can be attached to the low density foam layer, for example, either thermally or by the use of a suitable adhesive such as those described in the preceding paragraph.

5 The polyolefin used to make the foam is preferably the same as the high melt strength propylene polymer material having strain hardening elongational viscosity described in (2)(h).

10 Extruded foam sheets can be made by conventional techniques such as, for example, using a tandem extrusion line. The process includes mixing propylene resin having a high melt strength and high elasticity with a nucleating agent in a primary extruder, kneading the mixture, injecting a physical blowing agent into the mixture to form a foaming mixture, transferring the foaming mixture to a secondary extruder, mixing and cooling the foaming mixture, and extruding the foaming mixture through an annular or flat die into a continuous foam sheet. Suitable blowing agents include hydrocarbons such as butane and isopentane, chlorinated hydrocarbons, 15 chlorofluorocarbons, nitrogen, carbon dioxide, and other inert gases.

20 Low density foam layers molded from foam beads can be made, for example, by making prefoamed beads by extruding a high melt strength polypropylene in the presence of a foaming agent such as, for example, pentane, hexane, dichlorotrifluoroethane and methylene chloride. One or more nucleating agents such as talc, colloidal silica, sodium bicarbonate or its blends with citric acid, and azodicarbonamide, can be added to the polymer before or during extrusion. The prefoamed beads are then thermoformed by sintering. A mold having the desired dimensions is filled with the prefoamed beads and the beads are heated by passing a hot pressurized gas such as superheated steam through the mold to obtain sintering and produce the finished article. 25

30 The composite materials can be used for making large structural parts, for example by pressure or melt thermoforming techniques. Examples of parts that can be made from these materials include co-extruded profiles; household appliance cabinets and door liners; hot tubs; and boat hulls and boat decks as well as boat engine covers, consoles, and hatches. The co-extruded laminate of our invention can be adhered (such as by suitable adhesive) to an extruded polymeric foam, preferably the hereinabove described polyolefin foam such as a polypropylene foam, it being understood that for a marine applications, and particularly for a boat hull, the foam can be selectively located at discrete locations on the interior hull surface to provide

discrete reinforcement, in single or multiple foam layers that can be overlapping, stepped or stacked. Also, an inner laminate(s) can be provided over all or part of such selectively located foam reinforcement to provide a marine structure, such as a boat hull or deck, which in this relevant part, can have an outer surface formed from a co-extruded laminate(s) of our invention, a supporting foam reinforcement layer(s), and one or more inner co-extruded laminate(s). The latter laminates need not be the same composition as the laminate for the exterior hull or deck surface that may require high gloss and other properties. If loads are low, it is possible that a hull or deck may need just selective reinforcement, although the foam layer(s) can be adhered against the complete inner surface of the marine structure (hull or deck). The particular combination of materials used is determined by the properties desired in the thermoformed part.

Now, with reference to the appended figures, in Figures 1 and 2, foam core 30 is constructed from an expanded polypropylene, which forms bead like cells 32. Foam core 30 has a first surface and a second surface. An adhesive 28, such as a hot melt spray polypropylene adhesive, is provided to allow top skin 22 to adhere or bond to the first surface of foam core 30. In lieu of polypropylene, adhesive 28 can be an epoxy.

As seen in Figure 1, a bottom or back skin 36 can be attached or bonded to the second surface of foam core 30, preferably by a polypropylene adhesive 34 which can be the same as adhesive 28. Back skin 36 helps to prevent foam core 30 from cracking. Though not preferred, Figure 2 illustrates composite structure 20 without a back skin 36, and thus also without adhesive 34. Preferably, top skin 22, foam core 30, back skin 36 and adhesives 28 and 34 are all polypropylene based to provide a one hundred (100%) percent recyclable composite structure 20.

Figure 3 illustrates a multi-layer extruded polypropylene foam core 130. Top skin 122 and/or back skin 152 can be attached to foam core 130 through a welding or bonding process in lieu of adhesives (See Figure 7 and 8). Figure 7 illustrates top skin 122 and the back or inner skin 152 both attached to foam core 130 by fusing or bonding, while in Figure 8 only a top skin 122 is provided and fused with foam core 130. However, it should be understood that the polypropylene adhesives 128 and 150 can also be utilized for attaching skins 122 and 152, respectively, to extruded foam core 130 (See Figures 4 and 5). Adhesives 128 and 150 are similar to adhesives 28 and 34 discussed above for the first embodiment of the present invention.

Extruded foam core 130, preferably, varies in density to provide a composite foam core 130. The density of each layer which forms foam core 130 is determined by the amount of air which was entrapped within the specific layer during its construction. The more expanded the cells of the layer are, the lower the density of such layer. To construct a composite polypropylene foam core, such as foam core 130, of varying densities, the multiple density foam layers are fused or bonded together, similar to the fusing or bonding of extruded foam core 130 to top skin 122 and back skin 152.

Preferably, the various densities of the composite foam core 130 are arranged such that the lowest density foam layer is provided at the center of composite core 130 and the varying density foam layers of core 130 are fused together and extend outward from the center in numerical order (i.e. lowest density layer at center of foam core 130, highest density layer at outer surface of foam core). As seen in Figure 3, outer foam layers 132 and 136 are of a higher density as compared to the density of middle layer 140.

Foam core 130 is shown of consisting of three foam layers fused together to form a composite extruded polypropylene foam core 130. However, it should be understood that the present invention is not limited to a composite foam core consisting of three layers and any number of layers may be utilized, as may be necessary and are considered within the scope of the invention.

As seen in Figure 3, as the density for the foam layers gets higher the cells are brought closer together, i.e. compare extruded cells 134 of outer layer 132 and cells 138 of outer layer 136 with cells 142 of middle layer 140. Each layer of foam core 130 is preferably constructed from of an extruded polypropylene. The desired thickness for foam core 130 is achieved by the fusing of a plurality of layers necessary to reach the chosen thickness value.

Figure 6 illustrates an extruded foam core 230 which consist of a single polypropylene layer having a consistent density throughout as shown by cells 232. Though foam core 230 is shown only attached to top skin 122 by adhesive 128 it should be understood that foam core can also be attached to back skin 152 by a polypropylene adhesive. Furthermore, foam core 230 can also be fused or bonded to top skin 122 or back skin 152 similar to the described above for foam core 130. Accordingly, though not preferred, a single layer extruded foam core 230 can be substituted for multi-layer composite foam core 130 in appropriate circumstances.

Preferably, in all embodiments, the densities of top skin and back skin are relatively higher than the density of foam core 230. As to foam core 130, the densities of top skin 122 and back skin 152 are relatively higher than the densities of outer layers 132 and 134 of foam core 130, which in turn are relatively higher than middle layer 140 of foam core 130. Providing higher density outer skins and a low density core 30, 130 or 230, helps to reduce costs, while providing desired mechanical properties, such as a high shear gradient between the center and outside of the material. Top skin 122 and back skin 152 are constructed similar to top skin 22 and back skin 36 discussed for the first embodiment of the present invention.

As seen in Figures 9 and 10, top skin 122 is shown slightly bowed as a desired shape. To have foam core 130 correspond to the shape of top skin 122, slits or cuts 160 are provided through foam core 130 at selected or random intervals. Preferably, back skin 152 is attached to foam core 130, as discussed above, prior to providing slits 160, in order to keep foam core 130 together. After slits 160 have been provided, foam core 130 and back skin 152 can be bowed to correspond to the shape of top skin 122. Once foam core 130 is bowed or bent to its desired shape it is attached to top skin 122 either by adhesives 128 (Figure 9) or fusing (Figure 10), similar to the embodiments described above.

As the entire composite structure 20 or 120 is primarily constructed from polypropylene, the composite is one hundred (100%) recyclable and eliminates concerns of toxicity. Furthermore, the present invention provides for a novel method of constructing composite structure 20 or 120. The present invention is also novel with respect to bonding or fusing a foam core to a weatherable polypropylene sheet, such as top skin 22 or 122. Thus, the present invention overcomes previous problems of bonding or using a foam core to a polypropylene sheet.

Composite structure 20 or 120 can be utilized as a replacement to fiberglass and other materials in many applications, including, but not limited to, boat hulls and decks, camper tops, coolers, etc. Furthermore, composite structure 20 or 120 absorbs a relatively higher amount of energy as compared to other materials such as fiberglass or wood. Substituting composite structure 20 or 120 for the wood or fiberglass, allows composite structure 20 or 120 to absorb fifty (50%) to sixty (60%) percent of the wave slap and impact energy, to thereby provide a relatively more comfortable and smooth boat ride. The use of composite structure 20 or 120 also reduces the amount of maintenance necessary as compared to fiberglass and improves durability.

Structure 20 or 120 also has better long term cosmetically as compared to fiberglass. In addition to fiberglass and wood, structure 20 or 120 can also be utilized as a replacement for composite structures containing polyurethane or similar structures.

The co-extruded laminates can be adhered to a foam core to provide a thermoformed composite, as disclosed in U.S. Patent No. 5,916,672, the complete disclosure of which is incorporated herein by reference.

Examples

The test methods used to evaluate the properties of molded specimens were:

10	Room temperature (r.t.) Izod impact	ASTM D-256A
	Flexural modulus	ASTM D-790 86
	Flexural strength	ASTM D-790-86
	Tensile strength	ASTM D-638-89
	Elongation at break	ASTM D-638-89
15	Melt flow rate, 230°C, 2.16 kg	ASTM 1238
	Rockwell hardness	ASTM D-785, R scale
	Plate impact	ASTM D-3763-93

All gloss readings were taken with a 60 degree gloss meter from a smooth (ungrained) sample. A gloss value of 50 or more was considered to be acceptable. In this specification, all parts and percentages are by weight unless otherwise noted.

Example 1

This example describes the preparation and physical testing of a graft copolymer useful for making layer (1) of the laminate of this invention. The graft copolymer was made from a propylene homopolymer as the backbone polymer, to which was grafted a methyl methacrylate-methyl acrylate copolymer.

In this and the following examples the propylene homopolymer used as the backbone polymer of the graft copolymer had the following properties: spherical form, melt flow rate (MFR) of 9 g/10 min (ASTM D-1238, 230°C, 2.16 kg), a porosity of 0.45 cm³/g, and a molecular weight MW of 170,000. The monomers were grafted onto the polypropylene backbone at a grafting temperature of 237°F using the previously described peroxide-initiated graft polymerization process. Ninety-five

parts by weight of total monomers were added per 100 parts of polypropylene, of which 4.4% was methyl acrylate. Lupersd PMS (50% t-butylperoxy-2-ethyl hexanoate in mineral spirits), commercially available from Elf Atochem, was used as the peroxide initiator. The monomers were fed at a combined rate of 1 pph/min for 95
 5 minutes. A monomer to initiator molar ratio of 120 was used. The temperature was then raised to 284°F for 120 min under a nitrogen purge.

The graft copolymer was then blended with a broad molecular weight distribution polypropylene (BMWD PP) having a polydispersity index of 7.4, a MFR of 1 g/10 min. and xylene solubles at room temperature of 1.5%, commercially
 10 available from Montell USA Inc. The amount of BMWD PP used for each sample is given in Table 1. Enough BMWD PP was added to adjust the effective add level to the amount of monomer per hundred parts of polypropylene indicated in Table 4.

Engage 8150 ethylene/octane-1 copolymer having an octene-1 content of 25%, commercially available from Du Pont-Dow Elastomers, was added as an
 15 impact-modifier in the amounts shown in Table 1.

A UV stabilizer master batch was added to the formulation in an amount of 1.13% by weight. The master batch consisted of 0.25% Tinuvin 770 bis(2,2,6,6-tetramethyl-4-piperidiny)sebacate stabilizer; 0.30% Tinuvin 328 2-(hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole stabilizer; 0.25% Chimassorb
 20 119 1,3,5-triazine-2,4,6-triamine, N,N'-(1,2-ethanediylbis[N(3-[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl)amino]propyl)]-[N,N'-dibutyl-N',N''bis(1,2,2,6,6-pentamethyl-4-piperidiny) stabilizer; 0.25% Irganox B-215, a mixture of 1 part Irganox 1010 tetrakis[methylene(3,5-di-tert [butyl-4-
 25 hydroxyhydrocinnamate))]methane antioxidant and 2 parts Irgafus 168 tris(2,4-di-tert-butylphenyl) phosphite stabilizer, all commercially available from Ciba-Geigy Corporation, and 0.10% calcium stearate, based on the total weight of the composition.

3119 Ampacet 110499 (60% weatherable TiO₂ in an ethylene/methyl acrylate
 30 copolymer), commercially available from Ampacet Corporation, was also added in an amount of 1.67%.

The samples were compounded on a 40 mm co-rotating, intermeshing twin screw Werner & Phleiderer ZSK extruder at a barrel temperature of 220°C, a screw speed of 450 rpm, and a throughput rate of 210 lb/hr.

Compounded samples were dried at 80° for at least 4 hours prior to molding to remove moisture. Test specimens 8.5" long, ½", wide in the test region, and 1/8" thick were used for all of the physical property measurements. Test bars were produced on a 5 oz Battenfeld injection molding machine at a barrel temperature of 490°F and a mold temperature of 150°F.

The results of the property evaluations for each formulation are given in Table

1. In Table 1, Tot. E is total energy, and J is joules.

Table 1

Sample Number	1	2	3	4	5
Graft copolymer (%)	80.07	78.00	63.14	59.78	39.43
Effective Polymerized Monomer Add Level (pph)	70	70	50	50	30
BMW PP (%)	14.67	14.28	29.14	27.58	43.02
Rubber (%)	2.46	4.92	4.92	9.84	14.75
Stabilizer Master Batch (%)	1.13	1.13	1.13	1.13	1.13
Pigment (%)	1.67	1.67	1.67	1.67	1.67
MFR (230°C, 3.8 kg) g/10 min.	2.7	2.4	2.5	2.7	2.9
Flexural modulus, kpsi	300	291	280	244	210
Flexural strength, psi	8459	8234	7961	6914	5951
Tensile strength, psi	5353	5158	5082	4558	4209
Elongation to break (%)	12	16	17	56	226
Rockwell hardness (R)	101	100	98	90	82
Plate Impact, 23°C (J)	32.9	36.2	41	47.5	49.1
0°C (J)	2.5	16.8	18.3	38.3	50
-10°C (J)		10.4	12.9	37.1	55.4
-20°C (J)					54.8

Example 2

This example describes the preparation and physical testing of a material suitable for use as layer (2) of the laminate of this invention. The material was a

mixture of a high melt strength propylene polymer material (HMS PP) and one or more polyolefin materials.

HMS PP 1 was a propylene homopolymer having a MFR of 5-10 g/10 min. commercially available from Montell USA Inc. The high melt strength propylene polymer material was prepared by irradiating a propylene homopolymer having a nominal MFR of 1 g/10 min at a dose of ~ 6 Mrad using the irradiation process described previously.

HMS PP 2 was a propylene homopolymer having a MFR of <5 g/10 min. commercially available from Montell USA Inc. The high melt strength propylene polymer material was prepared by irradiating a propylene homopolymer having a nominal MFR of 0.6 g/10 min at a dose of ~9 Mrad using the irradiation process described previously.

Polyolefin material 1 was a heterophasic polyolefin composition comprising a propylene homopolymer impact-modified with an ethylene/propylene copolymer rubber, the total polymerized ethylene content of the composition being 8.9%. The material is commercially available from Montell USA Inc.

Polyolefin material 2 was a heterophasic polyolefin composition comprising a propylene homopolymer impact-modified with an ethylene/propylene copolymer rubber, the total polymerized ethylene content of the composition being 8.8%. The material is commercially available from Montell USA Inc.

Polyolefin material 3 was a propylene polymer material commercially available from Mordell USA Inc. comprising (a) 33% of a propylene-ethylene random copolymer having an ethylene content of 3.3% and an isotactic index, defined as the xylene insoluble fraction, of 94, (b) 6.5% of a semi-crystalline ethylene propylene copolymer that is insoluble in xylene at room temperature, and (c) 60.5% of an ethylene-propylene copolymer that is soluble in xylene at room temperature.

A stabilizer package consisting of 0.15% calcium stearate and 0.3% Irganox B-225 antioxidant, based on the total weight of the sample, was also added. B-225 antioxidant is a blend of 1 part Irganox 1010 antioxidant and 1 part Irgafos 168 stabilizer, commercially available from Ciba Geigy Corporation.

The samples were compounded on a 40 mm co-rotating, intermeshing twin screw Werner & Phleiderer ZSK extruder at a barrel temperature of 250°C, a screw speed of 350 rpm, and a throughput rate of 150 lb/hr for Sample 1 and 220 lb/hr for

Sample 2. Sample 3 was compounded on a 92 mm co-rotating, intermeshing twin screw extruder at a barrel temperature of 390°F, a screw speed of 225 rpm, and a throughput rate of 1800 lb/hr.

Test bars for physical property measurements were molded as described in Example 1.

The results of the property evaluations for each formulation are given in Table 2.

Table 2

Sample Number	1	2	3
HMS PP 1 (%)	19.91	19.91	—
HMS PP 2 (%)	—	—	19.92
Polyolefin Material 1 (%)	79.64	—	—
Polyolefin Material 2 (%)	—	59.73	69.72
Polyolefin Material 3 (%)	—	19.91	9.98
Ca Stearate (%)	0.15	0.15	0.1
Antioxidant (%)	0.3	0.3	0.3
MFR @ 230°C, 2.16 kg (g/10 min)	1.1	3.0	1.9
Flexural Modulus, kpsi	179	126	164
Flexural Strength, psi	5138	3633	4670
Tensile Strength, psi	4344	3323	3863
Elongation to Break (%)	230	680	394
23°C Izod Impact (ft-lb/in)	18.9	15.1	11.9
Plate Impact, 23°C (J)	35.1	32.2	40.3
0°C (J)	11.2	38.9	44.1
-10°C (J)	—	43	37.9
-20°C (J)	3.2	36.9	20.2

Example 3

Preparation of a co-extruded laminate was simulated in the laboratory using a Boy 203 injection molder. Disks 4" in diameter and 33 mils thick were molded from each graft copolymer formulation at a barrel temperature of 510°F and a mod

temperature of 175°F (layer (1)). The disks were then inserted into a mold cavity that was 1/8" deep and a layer (2) containing the high melt strength propylene polymer material was injected into the cavity at 520°F to produce 0.125 inch thick laminates. The samples used for each layer are given in Table 3.

5 Rheometric impact measurements were made on the laminates as indicated in Table 3. Descriptions of the graft copolymer formulations in layer (1) are found in Example 1. Descriptions of the HMS PP formulations in layer (2) are found in Example 2. The same tests were conducted on comparative samples consisting of glass fiber-reinforced polyester (FRP), and ABS capped with ASA. The results are
10 given in Table 3.

Table 3

Graft Copolymer Sample No.	HMS PP Sample Number	R.T.	0°C	-20°C
		Tot. E (J)	Tot. E (J)	Tot. E (J)
1	1	29.7	18.7	—
2	1	29.8	24	—
3	1	33	26.8	—
1	2	31.2	33.4	—
2	2	31.6	36.6	—
3	2	32.5	37.1	—
4	2	22.8	25.9	—
5	2	26.3	29.9	23.8
FRP		14.1	10.6	—
ASA/ABS		18.6	20.7	8.3

30 Example 4

This example describes the preparation of a co-extruded laminate in which layer (1) contained a methyl methacrylate/methyl acrylate-grafted propylene

homopolymer and layer (2) contained a mixture of polyolefin materials 2 and 3 and high melt strength propylene polymer material 2.

The graft copolymer was prepared as described in Example 1 and was then blended with the BMWD PP described in Example 1. The amounts of graft copolymer and BMWD PP are given in Table 4. Enough BMWD PP was added to adjust the effective add level to the amount of monomer per hundred parts of polypropylene indicated in Table 4.

Engage 8150 ethylene/octane-1 copolymer, commercially available from Du Pont-Dow Elastomers, was added as an impact modifier in the amounts shown in Table 4. The UV stabilizer master batch used in Example 1 was added to Samples 1-5 in an amount of 1.12% by weight. A UV stabilizer master batch consisting of 19.05% Irganox LC20 FF, which is a mixture of 1 part Irganox 1010 antiooddant and 1 part Irgafos 12 stabilizer (2,2',2"-nitriilo triethyl-tris[3,3',5,5'-tetra-tert butyl-1,1'-biphenyl-2,2'-diyl] phosphite), commercially available from Ciba Geigy Corporation; 9.52% Patonic 1240, modified calcium salt of lactic add, commercially available from the Patco Polymer Additives Division of American Ingredients Company; 28.57% Tinuvin 328, commercially available from Ciba Geigy Corporation; 23.8% Tinuvin 770, commercially available from Ciba Geigy Corporation, and 23.8% Chimassorb 119, commercially available from Ciba Geigy Corporation, was added to Sample 6 in an amount of 1.03% by weight.

A pigment package consisting of 81.22% 3113 R960 white PW6 TiO₂ pigment, commercially available from E. I. Du Pont de Nemours & Company; 18.26% Advawax 280 N,N'-ethylenebis(stearamide) pigment dispersion aid, commercially available from Morton International; 0.017% 2607 2GLTE YELPY 109, commercially available from Ciba-Geigy Corporation, and 0.503% 3309 GOLD.19P.BLK12, commercially available from Shepherd Chemical Company, was also added in an amount of 1.14%.

Samples 1-5 were compounded as described in Example 1. Sample 6 was compounded on a 40 mm co-rotating, intermeshing twin screw Werner & Phleiderer ZSK extruder with a flat profile at a barrel temperature of 220.C, a screw speed of 430 rpm, and a throughput rate of 225 lb/hr.

Compounded samples were dried at 80°C for at least 4 hours prior to molding to remove moisture. Test bars for physical testing were produced as described in Example 1.

The results of the property evaluations are given in Table 2.

TABLE 4

Sample Number	1	2	3	4	5	6
Graft Copolymer (%)	79.47	77.41	62.66	59.34	39.14	77.33
Effective polymerized monomer content (pph)	70	70	50	50	30	70
BMWD PP (%)	14.56	14.18	28.93	27.37	42.7	14.3
Rubber (%)	2.44	4.88	4.88	9.76	14.64	4.92
Stabilizer master batch (%)	1.12	1.12	1.12	1.12	1.12	1.03
Pigment package (%)	2.41	2.41	2.41	2.41	2.41	2.41
MFR @ 230°C, 3.8 kg (g/10 min)	3	3.2	3	3.1	3.3	4.9
Flexural modulus (kpsi)	285	263	258	218	169	264
Tensile strength (psi)	5255	4893	5012	4241	3684	485
Elongation to break (%)						36
23°C Izod impact (ft-lb/in)	1.4	1.8	1.7	2.9	16.5	1.4
Flexural strength (psi)	8335	7614	7591	6280	4994	7397
Rockwell hardness (R)	101	96	97	85	70	

Layer (2) consisted of a mixture of high melt strength propylene polymer material 2, polyolefin materials 2 and 3, calcium stearate and B-225 antioxidant, commercially available from Ciba-Geigy Corporation. The high melt strength
5 propylene polymer material and the polyolefin materials are described in Example 2. The amounts of each component of the formulation are given in Table 5.

The samples were compounded as described in Example 2.

Test bars for physical property measurements were molded as described in Example 1.

10 The results of the property evaluations are given in Table 2, Sample 3.

Co-extruded laminates were produced from Sample 1 of the graft copolymer formulations and the high melt strength propylene polymer formulation described above. The Extrusion was carried out using a primary extruder having a 6 inch single screw and a barrel temperature of 420°F (high melt strength propylene polymer layer)
15 and a co-extruder having a 4.5 inch single screw and a barrel temperature of 465°F (graft copolymer layer). The die was a coat hanger single manifold die with a die gap setting of 350 mils. The combined throughput rate was 1800 lb/hr.

The results of the physical testing measurements on the co-extruded laminate are given in Table 5.

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25

30

Table 5

Laminate Top Layer	
Sample No.	1
Graft Copolymer (%)	79.47
Effective Polymerized Monomer	70
Add Level (pph)	
BMWD PP (%)	14.56
Rubber (%)	2.44
Stabilizer Master Batch (%)	1.12
Pigment (%)	2.41
Laminate Bottom Layer	
Sample No.	3
HMS PP 2 (%)	19.92
Polyolefin Material 2 (%)	69.72
Polyolefin Material 3 (%)	9.96
Ca Stearate (%)	0.1
Antioxidant (%)	0.3
Laminate Thickness (mils)	233
Laminate Flexural Modulus (ksi)	200
Laminate Flexural Strength (psi)	6182
Gloss (60 deg) (%)	86
Rockwell Hardness (R)	
23°C Plate Impact (J)	79
0°C (J)	91
-10°C (J)	76
-20°C (J)	23

Example 5

This example describes the preparation of a co-extruded laminate in which layer (1) contained a methyl methacrylate/methyl acrylate-grafted propylene homopolymer and layer (2) contained a mixture of polyolefin materials 2 and 3 and high melt strength propylene polymer material 2.

The graft copolymer was prepared as described in Example 1 and was then blended with the BMWD PP described in Example 1. The amounts of graft copolymer and BMWD PP are given in Table 6. Enough BMWD PP was added to adjust the effective monomer add level to 70 parts per hundred parts of propylene homopolymer. The UV stabilizer master batch described in Example 1 was added to Samples 1 and 2, and the stabilizer master batch described in Example 4 was added to Sample 6 in the amounts shown in Table 6.

Engage 8150 ethylene/octane-1 copolymer, commercially available from DuPont-Dow Elastomers, was added as an impact modifier in the amounts shown in Table 6. The pigment described in Example 4 was added in an amount of 2.41% by weight.

Samples 1 and 2 were compounded as described in Example 1. Sample 6 was compounded as described in Example 4.

Layer (2) consisted of a mixture of high melt strength propylene polymer material 2, polyolefin materials 2 and 3, calcium stearate, B-225 antioxidant, commercially available from Ciba-Geigy Corporation, and TiO₂ pigment. The high melt strength propylene polymer material and the polyolefin materials are described in Example 2. The amounts of each component of the formulation are given in Table 6.

The samples were compounded as described in Example 2 for Sample 3.

Co-extruded laminates were produced from Samples 1, 2, and 6 of the graft copolymer formulations and the high melt strength propylene polymer formulation described above. The co-extrusion was carried out using a primary extruder having a 6 inch single screw and a melt temperature of ~390°F (high melt strength polypropylene layer) and a co-extruder having a 4" single screw and a melt temperature of ~430°F (graft copolymer layer). Both extruders were double vented and had a melt pump. For samples 1 and 2 the die was a coat hanger single manifold die with a die gap setting of 350 mils and the combined throughput rate was 1000

lb/hr. For Sample 6, the die was a dual manifold die with a die gap setting of 375 mile and the combined throughput rate was 1000 lb/hr.

The results of the physical testing measurements on the co-extruded laminates are given in Table 6.

Table 6

Laminate Top Layer				
Sample No.	1	1	2	6
Graft Copolymer (%)	79.47	79.47	77.41	77.33
Effective Polymerized Monomer Add Level	70	70	70	70
BMWD PP (%)	14.56	14.56	14.18	14.3
Rubber	2.44	2.44	4.88	4.92
Stabilizer Master Batch (%)	1.12	1.12	1.12	1.03
Pigment (%)	2.41	2.41	2.41	2.41
Laminate Bottom Layer				
HMS PP 2 (%)	19.92	19.92	19.92	19.71
Polyolefin Material 2 (%)	69.72	69.72	69.72	69.03
Polyolefin Material 3 (%)	9.96	9.96	9.96	9.86
Ca Stearate (%)	0.1	0.1	0.1	0.1
TiO ₂ (%)	-	-	-	1
Antioxidant (%)	0.3	0.3	0.3	0.3
Laminate Thickness (mils)	150	200	300	275
Flexural Modulus (kpsi)	115	188	157	215
Gloss (60 deg) (%)	89.5	90.5	87.6	87
Rockwell Hardness (R)	87.3	91.5	101.5	-
23°C Plate Impact (J)	41	78	155	147
0°C (J)	50.8	78.4	164.3	178.8

The instant invention has been shown and described herein in what is considered to be the most practical and preferred embodiment. It is recognized, however, that departures may be made therefrom within the scope of the invention and that obvious modifications will occur to a person skilled in the art.

WHAT IS CLAIMED IS:

1. An extruded laminate, comprising:
an extruded acrylic polypropylene outer layer; and
a polypropylene substrate attached to the acrylic polypropylene outer layer.
- 5 2. The extruded laminate of claim 1, wherein the polypropylene substrate has a density lower than a density of the extruded acrylic polypropylene outer layer.
3. The extruded laminate of claim 1, wherein the outer layer further includes an amorphous material to increase the impact strength of the outer layer.
4. The extruded laminate of claim 1, wherein the substrate is co-extruded with
10 the outer layer.
5. The extruded laminate of claim 1, wherein the outer layer has a high gloss surface.
6. The extruded laminate of claim 1 in combination with a structural member of a vehicle.
- 15 7. The extruded laminate of claim 6, wherein the vehicle is an automobile.
8. The extruded laminate of claim 6, wherein the vehicle is marine vessel.
9. The extruded laminate of claim 1 in combination with a household appliance.
10. The extruded laminate of claim 1 in combination with a hot tub.
11. A co-extruded thermoplastics laminate containing a polyolefin graft polymer
20 and one or more layers of polyolefin material.
12. The co-extruded thermoplastics laminate of claim 11, wherein the polyolefin graft polymer is an outer layer of acrylic polypropylene.
13. The co-extruded thermoplastics laminate of claim 12, wherein the polyolefin material is a low density polypropylene substrate.
- 25 14. The co-extruded thermoplastics laminate of claim 13, wherein the outer layer forms a thin glossy top coat having a first thickness and the substrate has a second thickness larger than the first thickness.

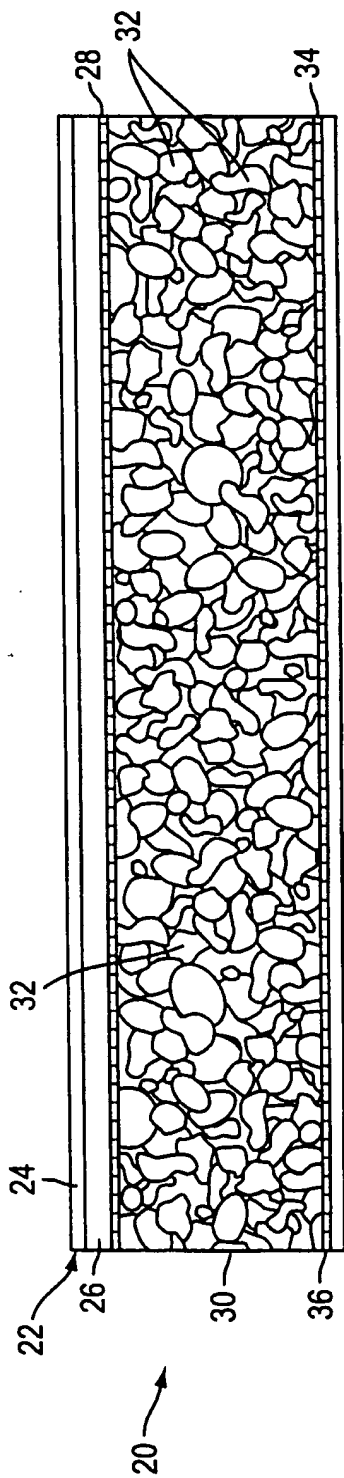


FIG. 1

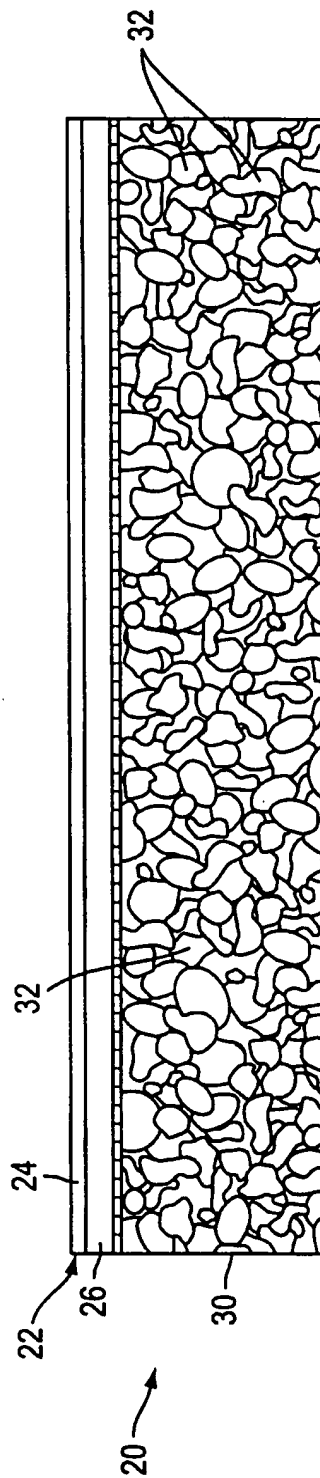
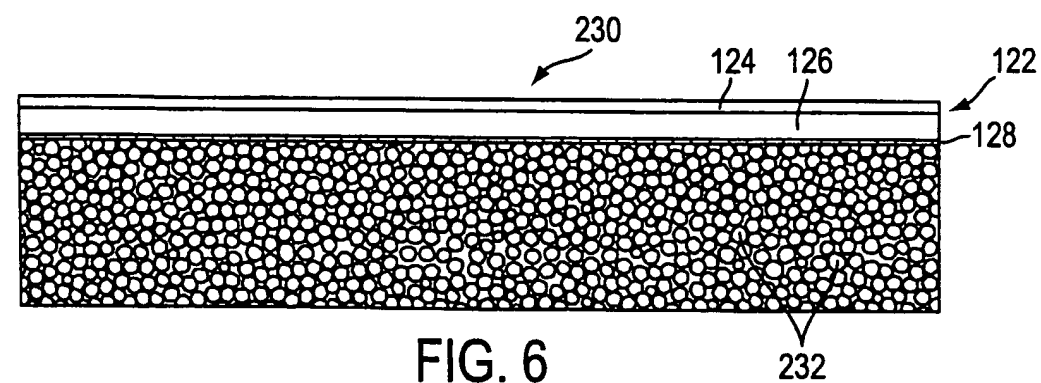
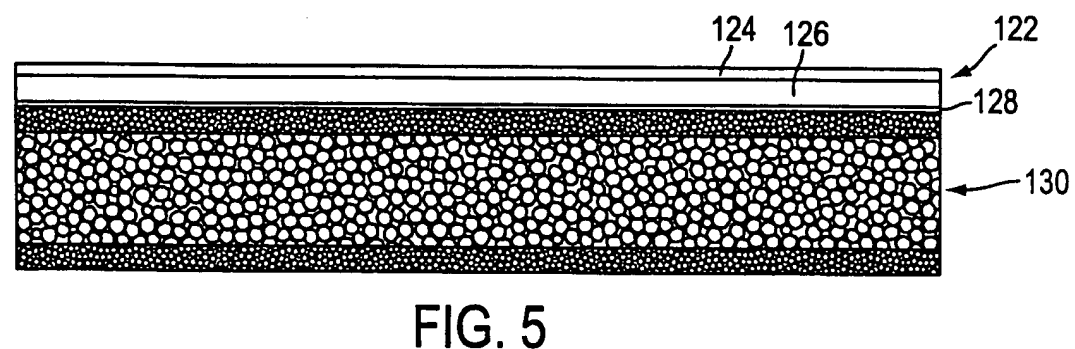
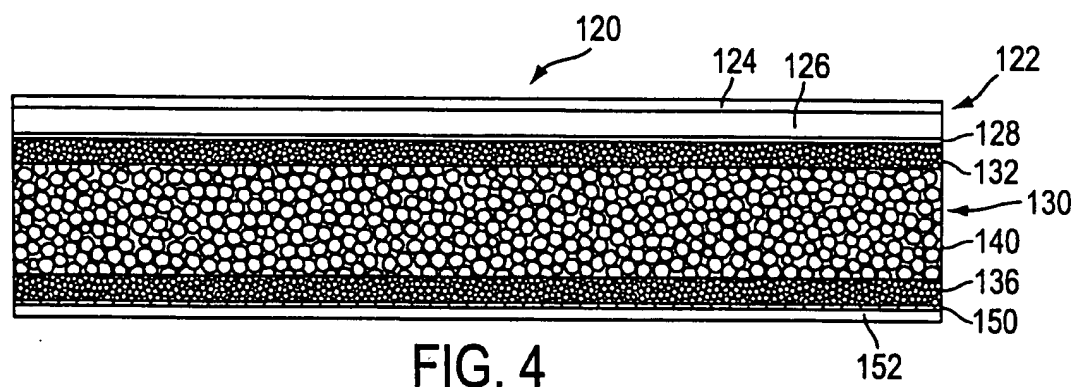
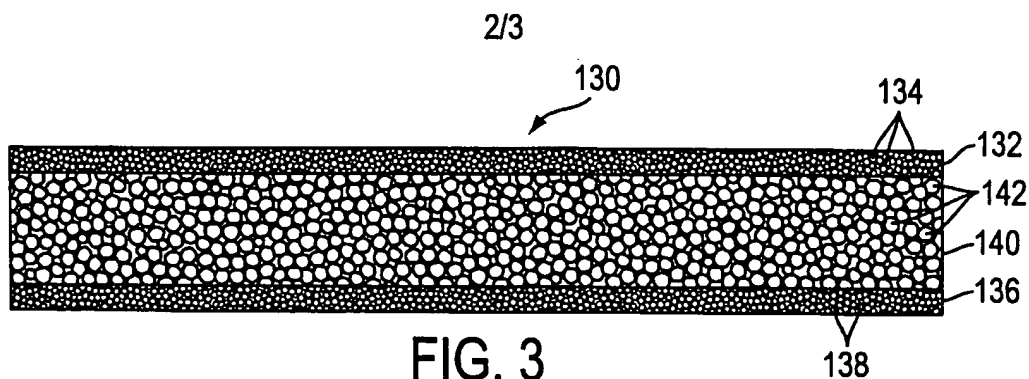


FIG. 2



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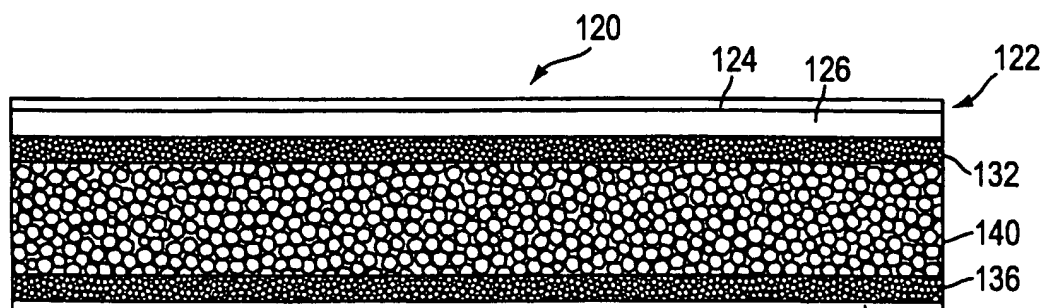


FIG. 7

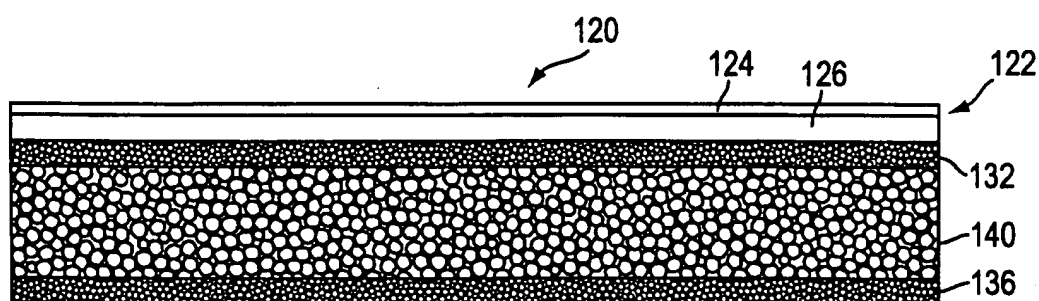


FIG. 8

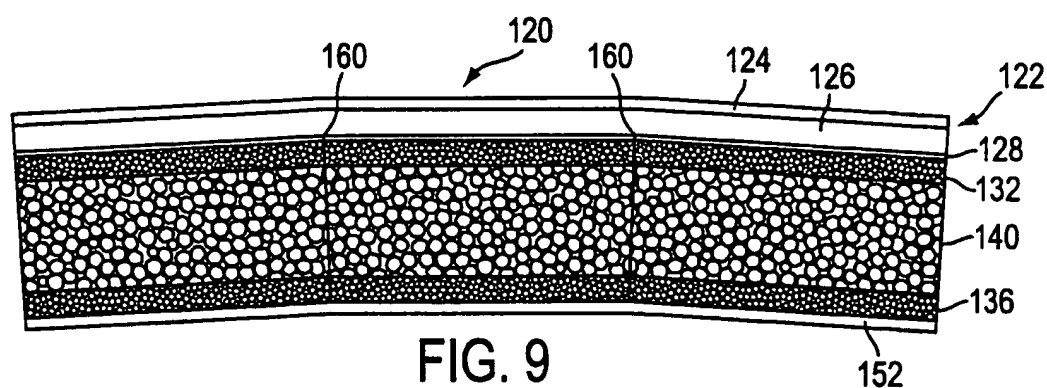


FIG. 9

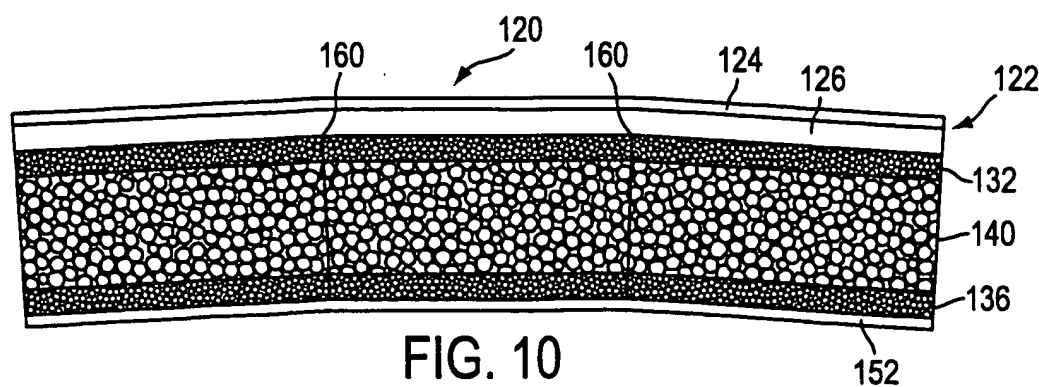


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/29642

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B32B 27/32

US CL : 428/218, 516

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/218, 516

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0

search terms: laminate, composite, extruded, extrusion, extrude, acrylic, polypropylene, substrate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,916,672 A (REEVES et al) 29 June 1999, see entire document.	1-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 DECEMBER 2000

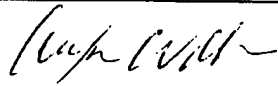
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